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Production and Characterization of Manganese Oxide-Based Electrodes for Anodic Oxidation of Organic Compounds

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Preliminary results concerning the fabrication and use of manganese oxide thin film electrodes are presented. Different deposition techniques were employed and compared in order to obtain enhanced anodic oxidation of organic pollutants. In particular, manganese oxide films were produced by cathodic electrodeposition from aqueous $KMnO_4$ solutions (Type-A), by anodic electrodeposition from aqueous $MnSO_4$ solutions (Type-B) and by thermal decomposition from alcoholic solutions (Type-C). All the films were grown on titanium foil covered with a thermally deposited ruthenium oxide inter-layer to ensure good electrical contact. In addiction to characterization by cyclic voltammetry (CV), X-Ray diffraction (XRD), and profilometric measurements, the electrodes were tested for the treatment of aqueous solutions containing the azo dye Reactive Violet 5 (RV5), as a model organic pollutant. The azo-dye degradation, conducted under galvanostatic conditions in an undivided reactor, was evaluated by UV–Vis measurements and COD analysis. In the presence of small concentration of NaCl, all electrodes exhibited good decolorization and COD reduction capability. The type-B electrodes showed the best performances. The Type-C electrodes accounted for anodes less performant with negligible formation of active chlorine.

1. Introduction

Treatment of industrial effluent using electrochemical techniques is becoming increasingly significant due to their versatility, high efficiency and “greener” approach (Comninellis and Chen, 2010). Nevertheless, electrochemical processes, often characterized by very complex reactions, request electrode materials with high efficiency and durability. Presently, the best materials involve the use of precious metals thus increasing costs and limiting the applicability of the electro-oxidation processes. A great effort is then devoted to investigate cheaper materials with comparable performances. Among these, manganese oxides (MnOx) materials represent an interesting family for electrode fabrication. These oxides show good electrocatalytic properties, low cost and availability, environmental compatibility and chemical stability. Up to now they are primarily used as cathodes in alkaline batteries (Kordesh and Weissenbacher, 1994), in lithium-ion batteries (Fergus, 2010) and supercapacitors (Wei et al, 2011) while fewer applications are reported regarding the electrochemical treatment of toxic compounds (Chen et al, 2012).

Many researchers are involved in the preparation of MnOx films and in the study of their electrochemical properties. These films are deposited on an appropriated support by several techniques: sol-gel (Chen et al, 2009), electrochemical deposition (Chou et al, 2006), electrostatic spray deposition (Nam and Kim, 2006) physical vapor deposition (Djurfors et al, 2005) and chemical bath deposition (Xia et al., 2009); the preparation method could significantly affects the electrode performance.

In a previous work (unpublished results) we have deposited MnOx films with good electrocathalytic properties on different metallic supports (Pt, Ni). However, the main limitation was a poor adhesion and an insufficient mechanical stability and durability of films except for those grown on Pt plate (which is not suitable under an industrial point of view).

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The aim of this work is to develop a dimensionally stable anode (DSA) with a MnOx film to be used in the electrochemical degradation of very stable or toxic pollutant compounds. To this aim, Reactive Violet 5 textile dye was selected as a model compound. This dye is a relatively new compound appreciated for its bright color and high fastness to bleaching, light and washing. It contains a vinyl sulphone group responsible for the binding with cellulosic fibers under alkaline conditions. There are few studies in the literature dealing with the degradation of this dye and the majority of these use bacterial colonies (Moosvi et al, 2005; Jain et al, 2012). Other treatments, including adsorption techniques on low cost material (Zuorro et al, 2013; Kyzas et al, 2013) and TiO_2 photocatalysis (Chung et al, 2009), have been further proposed.

In the experiments, MnOx films were formed on a Ti foil covered with a ruthenium oxide (RuOx) inter-layer to obtain a good adhesion and good electrical connection. Titanium was chosen for its chemical and mechanical stability, its good thermal resistance and lower cost compared to other materials. Moreover, as literature shows, RuOx is conductive and films deposited on titanium prevent passivation during electrolysis.

In this work several techniques for the synthesis of MnOx films were investigated: chemical deposition, electro-oxidation from aqueous solutions and electro-reduction from alcoholic solutions. All the samples were characterized by morphological and electrochemical analysis; in order to evaluate the efficiency of electrochemical treatment for decolorization and subsequent oxidation, electrolyses under galvanostatic conditions were conducted in a reactor without separation.

2. Experimental

2.1 Materials

Reagents were supplied by Sigma Aldrich and used without any further purification. Dye solutions were prepared by dissolving in distilled water 100 mg L^{-1} of RV5 of technical grade ($C_{20}H_{16}N_3Na_3O_{15}S_4$, MW 735.58 g mol^{-1}, CI 18097, Gammacolor Srl), with, if not differently specified, 0.5 M Na_2SO_4 as the supporting electrolyte and 0.01 M NaCl as chloride ion precursor.

2.2 Electrode preparation

Titanium sheets (99.6%, 1.5 cm x 1.5 cm) were rinsed by ultrasonic washing for 10 minutes with double distilled water and then with acetone. A RuO_2 interlayer was prepared using a thermal treatment by painting a 0,1M $RuCl_3$ isopropanolic solution on one side of the electrode. The electrodes were then calcinated in a muffle furnace for 5 min at 400°C. The treatment was repeated four times followed by a final 1 hour treatment at 450 °C.

The manganese oxide thin film was deposited by adopting three different synthetic routes:

1) cathodic electrochemical deposition (Type-A electrodes). The Ti-RuOx sheet prepared before was used as the cathode in an aqueous solution of 0.02 M $KMnO_4$. The galvanostatic electrolysis performed under galvanostatic conditions at a current density of 2 mA/cm^2, was conducted in an undivided cell of 30 mL volume, using a platinum foil as the anode and operating under conditions of room temperature with gentle agitation of the electrolytic solution, without performing pH control.

2) anodic electrochemical deposition (Type-B electrodes). The Ti-RuOx sheet described above was used as the anode in an aqueous solution containing both 0.005 M $MnSO_4$ and 0.01 M Na_2SO_4 (as supporting electrolyte). The potential, measured *versus* a saturated calomel reference electrode (SCE) as reference electrode, was initially kept constant at 0.5 V for 30 seconds. Then, a potential ramp from 0.5 V to 1.15 V at a scan rate of 5 mV/s, was applied in the undivided cell (volume of 30 mL), using a platinum foil as a cathode and operating in conditions of room temperature, without agitation and without pH control.

3) chemical deposition (Type-C electrodes). The procedure included the surface painting of the Ti-RuOx sheet described above with an ethanolic solution of 0.5 M $Mn(NO_3)_2$ followed by a 5 min treatment in a furnace at 350 °C. The whole cycle was repeated 4 times and completed by a 1 hour treatment at 400 °C.

2.3 Electrode characterization

XRD measures were conducted using a Philips Analytical XPERT Pro PW 3040 diffractometer with Cu Kα radiation (λ = 1.54056 Å), operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded in the 2θ range between 20° and 80°, with a step of 0.02° and a time of 2 s per step.

Surface roughness was assessed with a profilometer (3D Taylor Hobson Talyscan 150) equipped with a tracing diamond tip of 5 µm. The area scanned was 4 mm × 4 mm: 4001 points at a distance of 1 µm and 801 lines at a distance of 5 µm. A tracing speed of 1 mm/s was adopted. The following parameters were recorded and served to interpretation:

R_a: represents the arithmetical mean of the absolute deviations of the profile respect to the mean line.

R_{sk}: represents a symmetry factor of the profile with respect to the mean line; the prevalence of valleys or peaks determines a negative or positive R_{sk} value, respectively.
R_{ku}: represents the measure of sharpness of profile peaks.
Cyclic voltammetry (CV) experiments were performed at room temperature with a three-electrode cell of 10 mL volume consisting of the in-made anode, a Pt sheet as the counter electrode and a saturated calomel reference electrode (SCE). A AMEL 5000 potentiostat was used. The scan rate was 20 mV/s and scan range was from 0 to +1.5 V. In the following discussion, we will always refer to the second cycle as this is not influenced by accumulation or adsorption of substances during the initial waiting time, as it is the case for the first cycle. Where reported, the chloride concentration in solution was varied by adding NaCl.

2.4 RV5 Electrochemical degradation of reactive Violet 5 solutions

Electrolyses were performed under galvanostatic conditions at a current density of 200 A m^{-2} using a potentiostat AMEL 2051. The cell was an undivided glass reactor of 100 mL volume, kept at constant temperature and agitated with a magnetic stirrer. The cathode was a Pt sheet of 2.25 cm^2. The anodes tested were the in-made thin film MnOx oxide electrodes and, for a comparison, in a separate test a boron doped diamond electrode BDD (Adamant Technologies) was also used. All anodes had a total surface area of 2.25 cm^2. Tests were conducted at room temperature. The results from duplicate testing showed high reproducibility of active chlorine production, COD and efficiency in color removal.

2.5 Analytical methods and equipment

pH was measured by using a Crison GLP 421.
The color removal was assessed by measuring the absorbance decrease at the maximum wavelength (558 nm) with a PG Instruments T80+ UV/Vis spectrophotometer.
The chemical oxygen demand (COD) was determined according to standard methods based on acid digestion, reflux and spectrophotometric determination at wavelength 443 nm.
The active chlorine concentration was determined using the DPD (N,N-diethyl-p-phenylenediamine) reagent by colorimetric method at 510 nm wavelength.
The concentration of anions were determined using a Dionex 120 ionic chromatograph equipped with an IONPAC AS12A anionic column working in isocratic mode and a conductometric detector.
The removal efficiencies of color and COD removal were calculated using the following formula, where x_0 and x_t represent the initial and remaining value of the x variable at a given time:

$$R\ (\%) = \frac{(x_0 - x_t)}{x_0} * 100$$

3. Results

XRD patterns of the Type-C electrodes (for which the MnOx film had been obtained by thermal decomposition) enabled to identify the peaks corresponding to the Mn_2O_3 oxide (Figure 1), thus indicating that the Mn oxidation state was 3. It should mention that the low sensitivity of the diffractometer used has not allowed the identification nature of the Mn species existing in the films prepared by electrodeposition, probably due to the reduced thickness of these films.
As shown in Table 1, the three types of electrodes presented values of average roughness (R_a) rather comparable with a slightly higher value found in the sample prepared by thermal decomposition. However, R_{sk} and R_{ku} values differed significantly from each other, indicating that Type-A electrode presented extreme (R_{ku}>3 μm) peaks and valleys with a substantially symmetrical height distribution (R_{sk}=0 μm). Type-B electrode presented extreme (R_{ku}>3 μm) valleys (R_{sk}<0 μm), while Type-C electrode, being positively skewed (R_{sk}>0 μm), showed a prevalence of extreme (R_{ku}>3 μm) peaks or filled valleys (Gadelmawla et al, 2002).
The electrochemical behavior of electrodes was studied by cyclic voltammetry. Figure 2A exhibits the cyclic voltammograms of three electrodes covered with manganese oxide (Type-A, Type-B and Type-C), as well as of non-covered Ti and Ti-RuOx ones. It can be seen that the electrode prepared exclusively with RuOx film shows a typical response for this kind of electrode. The presence of MnOx film changes the electrochemical behaviour and the shapes of voltammograms show that these changes are strongly influenced by deposition technique. The Type-A electrode, in particular, shows a more intense voltammetric response, probably due to a very good surface activation.
Figure 2B compares the voltammograms for a Type-C electrode in solutions with and without sodium chloride. It can be observed that their shape is not influenced so much by the presence of chloride species; only a little shift of anodic peak potential towards more positive values is observed, with a very small diminution in the current response.

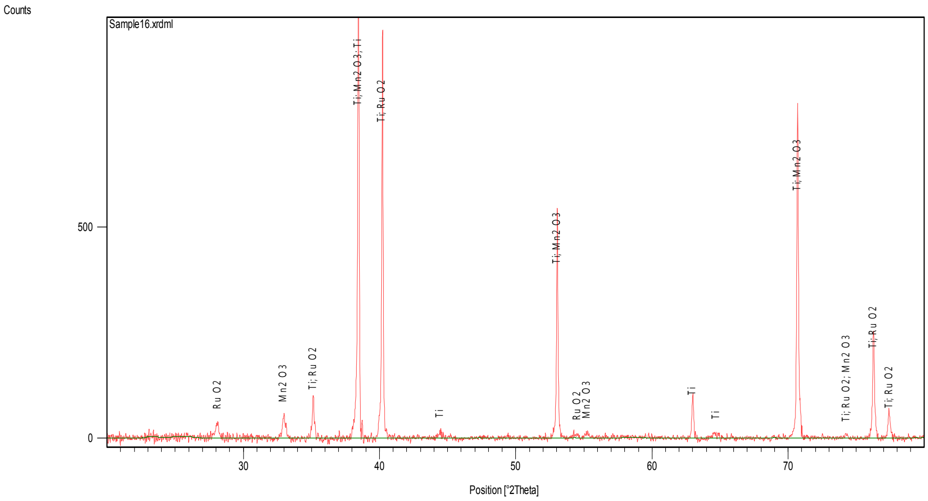

Figure 1: XRD pattern of Type-C electrode

Table 1: Roughness parameters of the electrode materials prepared

Anode	R_a (µm)	R_{ku} (µm)	R_{sk} (µm)
Type-A	0.41	5.99	0.00
Type-B	0.40	4.09	-0.65
Type-C	0.66	6.94	1.07

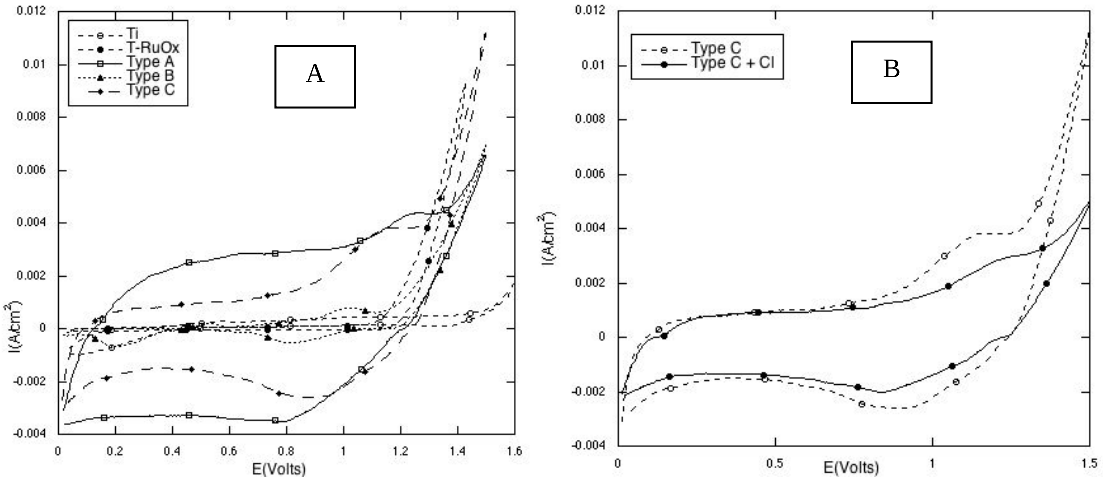

Figure 2: (A) Cyclic voltrammograms of Ti support, Ti with RuOx interlayer, Type-A electrode, Type-B electrode, Type-C electrode, immersed in a solution containing 100 gL^{-1} RV5, 0.5 M Na_2SO_4 and 0.01 M NaCl; (B) cyclic voltammograms of Type-C electrode immersed in the same solution with and without sodium chlorides.

To evaluate the performance of the three electrodes prepared, a preliminary series of electrolysis tests was conducted using a 100 mg L^{-1} aqueous solution of RV5, corresponding to a COD value of about 48 mg L^{-1} at a current density of 200 Am^{-2}. The same experiments were then repeated in the presence of 0.01 M NaCl in solution. Under the conditions adopted the cell potentials were always in the range 4.2-4.8 V and remained unchanged during the run.

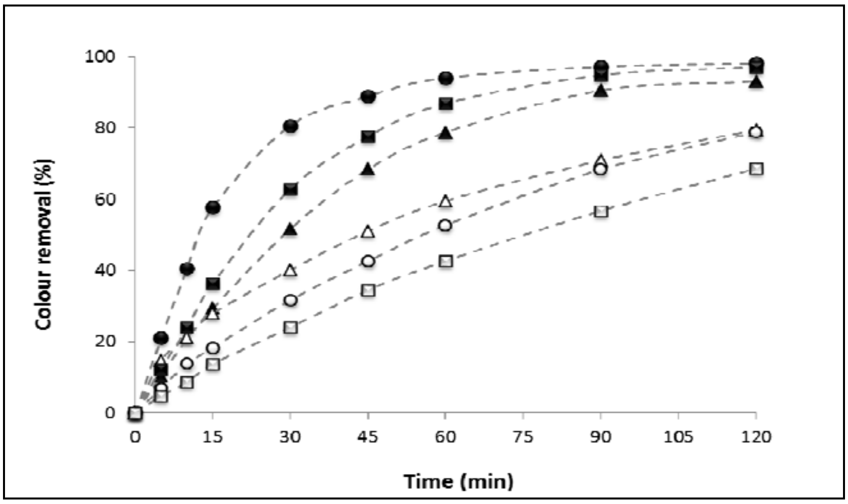

Figure 3: Evolution in time of the color removal of solutions containing RV5 = 100 mg L^{-1}, 0.05 M Na_2SO_4 without (empty symbols) and with 0.01M NaCl (full symbols) during electrolyses conducted at J = 200 A m^{-2}, T = 22 °C, non-corrected pH, with various electrodes: Type-A electrode (□), Type-B electrode (○), Type-C electrode (△).

The effect of chloride concentration on color removal as a function of the time is reported in Figure 3. As can be noted, the addition of chloride enhanced significantly the decolorization rate, due to occurrence of the indirect oxidation mediated by the electrogenerated active chlorine that selectively attacks the dye chromophore structure (Montanaro and Petrucci, 2009). In particular, considering the time needed to halve the initial dye concentration (t_{50}), it can be noted that the Type-B electrode (anodically deposited film) requires only 12 minutes, while 22 and 29 minutes are required to Type-A electrode (cathodically deposited film) and Type-C electrode (film obtained via thermal decomposition). The different behavior exhibited by the electrode materials can be attributed to the production of different concentration of active chlorine.

Table 2: Results of removal of color and COD, as well as the active chlorine production after 120 minutes treatment in electrolyses conducted at J=200Am^{-2}, T=22°C, non-corrected pH

Anode	ΔCol (%)		ΔCOD (%)		Active Chlorine (ppm)	
	0.01 M Cl^-	0 M Cl^-	0.01 M Cl^-	0 M Cl^-	0.01 M Cl^-	0 M Cl^-
Type-A	97.2	68.6	36.2	18.7	20.5	n.d.
Type-B	98.7	78.7	73.2	17.11	180.5	n.d.
Type-C	89.6	79.5	23.5	22.3	3.6	n.d.

As reported in Table 2, at the end of the electrolysis treatment the most performant electrode was Type-B anode, which allowed the production of 180 ppm of active chlorine, while only 20.5 and 3.6 ppm were found when Type-B and Type-C electrode were used. The different tendency of electrogenerating active chlorine could be explained by a hypothesis that the three materials presented different overpotential values for gaseous chlorine evolution. Presumably, the negligible content of active chlorine produced by the materials prepared by chemical decomposition (Type C anode) is due to the greater thickness of the manganese oxide film, as confirmed by analysis of roughness of surface and XRD patterns. Certainly, the layer thickness contributes to isolate the active ruthenium oxide interlayer that thereby cannot interact with the electrolyte. The greater tendency to electrogenerate active chlorine of the electrode whose film is anodically deposited (Type B anode) could be due to the formation of superficial mixed Mn/Ru oxides. Further study are required to investigate this topic. The lack of experimental evidence resulting from the morphological characterization does not allow to corroborate this hypothesis.

The results obtained in the COD removal tests confirmed that the Type-C electrode was unaffected by the addition of chloride species in solution, while the anodes prepared by electrodeposition (both Type A and Type B) exhibited a great variability of the efficiency. In particular, without chloride in solution, the performance of Type-A electrode showed a consistent deceleration enabling the attainment of only 18.7% removal, while that of Type-B anode dropped from 73.2% to a value substantially similar to those obtained with the others electrodes.

Preliminary analyses regarding evolution during electrolysis of the anionic species showed that the electrogeneration of active chlorine occurred without promoting chlorate or perchlorate production, thus showing interesting potential for applications to decolorization of dye-containing wastewaters.

4. Conclusions

Manganese oxide thin films are promising electrode materials for anodic oxidation of wastewaters containing organic compounds. Three different methods of deposition were tested and compared. Mechanically, chemically and electrically stable anode materials were prepared, characterized and tested in the degradation of solutions containing RV5 dye. The electrodes showed different morphological characteristics and electrocatalytic properties depending on the deposition technique adopted. All the electrodes, in the presence of small concentration of chloride ion in solution, exhibited faster removal of color and COD with different production of active chlorine, without electrogenerating chlorates or perchlorates.

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